Lanthanide Triflate Catalyzed Imino Diels–Alder Reactions; Convenient Syntheses of Pyridine and Quinoline Derivatives

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Lanthanide triflate catalyzed imino Diels–Alder reactions of imines with dienes or alkenes have been developed. A new group of Lewis acids, lanthanide triflates, are quite effective for the catalytic activation of imines. Unique reactivities of imines which work as both dienophiles and azadienes under certain conditions have been revealed. Three-component coupling reactions between aldehydes, amines, and dienes or alkenes were successfully carried out by using lanthanide triflate as a catalyst to afford pyridine and quinoline derivatives in high yields. The Lewis acid catalysts were stable and kept their activity even in the presence of water and amines. A stepwise reaction mechanism for these reactions is suggested from the experimental results.

The imino Diels–Alder reaction is among one of the most powerful synthetic tools for constructing N-containing six-membered heterocycles, such as pyridines and quinolines.[1] Although Lewis acids often promote these reactions, more than stoichiometric amounts of the acids are required due to the strong coordination of the acids to nitrogen atoms.[1] Recently, we have found that lanthanide triflates [Ln(OTf)$_3$] are stable in water and achieve Lewis acid catalysis in aqueous solutions.[2,3] Lanthanide triflates coordinate to Lewis bases under equilibrium conditions, and thus activation of carbonyl compounds using a catalytic amount of the acid has been achieved. We expected that, based on the same consideration, the catalytic activation of imines would be possible by using lanthanide triflates.[4] In this paper, we describe the unique properties of a new type of Lewis acid, lanthanide triflates, and the full details of Ln(OTf)$_3$-catalyzed imino Diels–Alder reactions including a stepwise reaction mechanism.

Reactions of Imines with Dienes or Alkenes

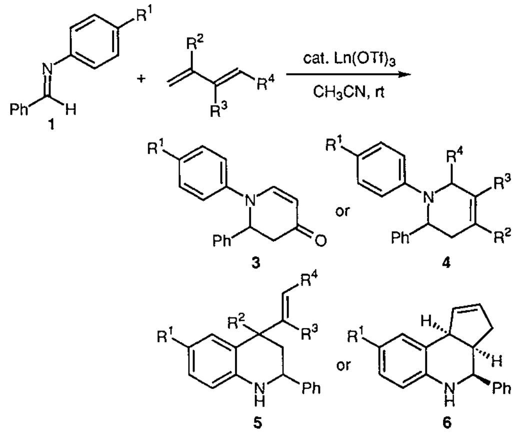
In the presence of 10 mol% ytterbium triflate [Yb(OTf)$_3$, a representative lanthanide triflate], *N*-benzilideneaniline (**1a**) was treated with 2-trimethylsiloxy-4-methoxy-1,3-butadiene (Danishefsky's diene, **2**)[5] in acetonitrile at room temperature. The imino Diels–Alder reaction proceeded smoothly to afford the corresponding tetrahydropyridine derivative in a 93 % yield (Table 1). The adduct was obtained quantitatively when scandium triflate [Sc(OTf)$_3$] was used as a catalyst. Imines **1b** and **1c** also reacted smoothly with **2** to give the corresponding adducts in high yields. Next, we performed the reaction of **1a** with cyclopentadiene under the same reaction conditions. It was found that the reaction course changed in this case and that a tetrahydroquinoline derivative was obtained in a 85% yield. In this reaction, the imine worked as an azadiene toward one of the double bonds of cyclopentadiene as a dienophile.[6,7] In the reactions of 2,3-dimethylbuta-1,3-diene, mixtures of tetrahydropyridine and tetrahydroquinoline derivatives were obtained.

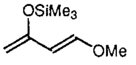
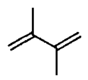
Other examples and effects of lanthanide triflates are shown in Tables 2 and 3, respectively. A vinyl sulfide, a vinyl ether, and a silyl enol ether worked well as dienophiles to afford tetrahydroquinoline derivatives in high yields.[8,9] As for the lanthanide triflates, heavy lanthanides such as erbium, thulium and ytterbium gave better results.

Three-Component Coupling Reactions between Aldehydes, Amines, and Dienes of Alkenes

One synthetic problem in the imino Diels–Alder reactions is the imines' stability under the influence of Lewis acids. It is desirable that the imines activated by Lewis acids are immediately trapped by dienes or dienophiles.[10] In 1989, a convenient procedure for the imino Diels–Alder

Table 1. Syntheses of Pyridine Derivatives Catalyzed by Ln(OTf)$_3$



R^1	Diene	Ln(OTf)$_3$ (mol%)	Product	Yield (%)
H (**1a**)		Yb(OTf)$_3$	**3a**	93 (99)[a)]
OMe (**1b**)	OSiMe$_3$ OMe	(10)	**3b**	82
Cl (**1c**)	**2**		**3c**	92
H (**1a**)		Sc(OTf)$_3$	**4a**+**5a**	54[b)]
OMe (**1b**)		(20)	**4b**+**5b**	71[c)]
Cl (**1c**)			**4c**+**5c**	50[d)]
H (**1a**)		Yb(OTf)$_3$	**6a**	85 (91)[e)]
OMe (**1b**)		(10)	**6b**	38
Cl (**1c**)			**6c**	85

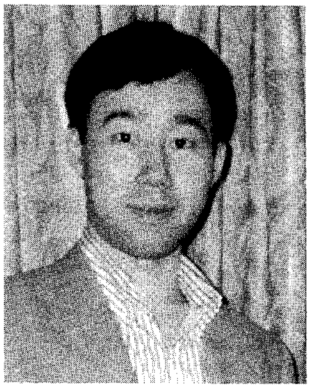
a) 10 mol% Sc(OTf)$_3$ was used. The reaction was carried out at 0 °C.
b) **4a** 37%, **5a** 17%. c) **4b** 8%, **5b** 63%. d) **4c** 37%, **5c** 13%.
e) 20 mol% Sc(OTf)$_3$ was used.

reaction of an aldehyde and a 1,3-diene with *N*-sulfinyl *p*-toluenesulfonamide via *N*-sulfonyl imine produced in situ, by using a stoichiometric amount of boron trifluoride–diethyl ether complex as a promoter was reported.[11]

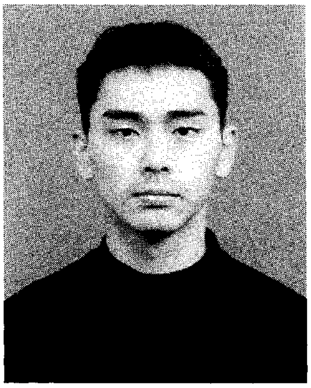
Bearing in mind the usefulness and efficiency of one-pot procedures, we examined three-component coupling reactions between aldehydes, amines, and alkenes via imine formation and imino Diels–Alder reaction by using lanthanide triflate as a catalyst.[12]

In the presence of 10 mol% of $Yb(OTf)_3$ and magnesium sulfate, benzaldehyde was treated with aniline and **2** successively in acetonitrile at room temperature. The three-component coupling reaction proceeded smoothly to afford the corresponding tetrahydropyridine derivative in an 80% yield. It is noteworthy that $Yb(OTf)_3$ kept its activity and effectively catalyzed the reaction even in the presence of water and the amine.[13] Use of $Sc(OTf)_3$ slightly improved the yield. Other examples of the three-component coupling reaction are shown in Table 4. In the reaction between benzaldehyde, aniline, and cyclopentadiene under the same reaction conditions, the reaction course changed and the tetrahydroquinoline derivative was obtained in a 56% yield. A vinyl sulfide and a vinyl ether worked well as dienophiles to afford tetra-

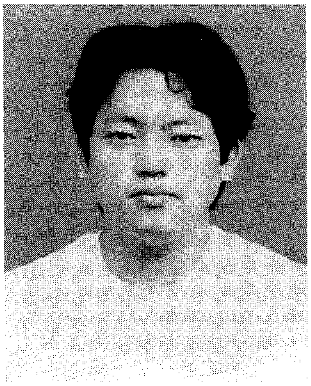
Biographical Sketches



Shū Kobayashi was born in 1959 in Tokyo, Japan. He studied chemistry at the University of Tokyo and obtained his PhD in 1988 under the guidance of Professor Teruaki Mukaiyama. He was a research fellow (Professor B.M. Trost at Wisconsin University, 1986) and a visiting professor of Université Louis Pasteur; Strasbourg, in 1993. He is now Associate Professor of Science at the University of Tokyo (SUT). He received the Chemical Society of Japan Award for Young Chemists in 1992. His research interests include development of new synthetic methods, development of novel catalysts, rare earth chemistry, and organometallic chemistry.

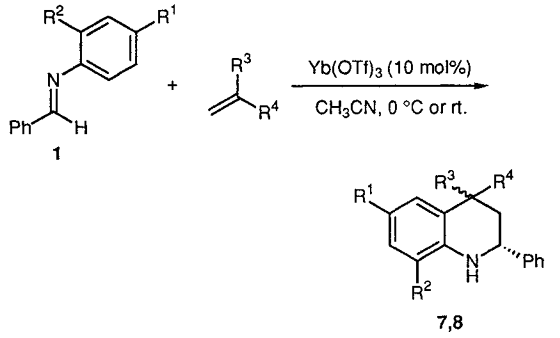


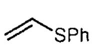
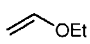
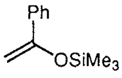
Haruro Ishitani was born in 1970 in Osaka. He received his MS degree at Science University of Tokyo (SUT) in 1995. He is currently pursuing his PhD in the Kobayashi group developing new rare earth catalysis.



Satoshi Nagayama was born in 1971 in Nagoya. He received his BS degree at Science University of Tokyo (SUT) in 1995. He is now a master course student and his research subject is to develop new lanthanide catalysts.

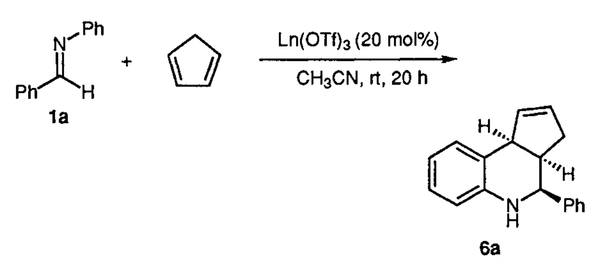
Table 2. Syntheses of Quinoline Derivatives Catalyzed by Ln(OTf)$_3$



R^1	R^2		Alkene	Product	Yield (%)	*cis/trans*
H	H	(1a)		7a	75	57/43
OMe	H	(1b)		7b	0	—
Cl	H	(1c)		7c	quant.	nd[a]
H	OMe	(1d)		7d	70	nd[a]
H	H	(1a)		8a	96	nd[a]
OMe	H	(1b)		8b	77	67/33
Cl	H	(1c)		8c	95	nd[a]
OMe	H	(1b)		9	quant.	83/17[b]

a) Not determined. b) Relative configration assignment was not made.

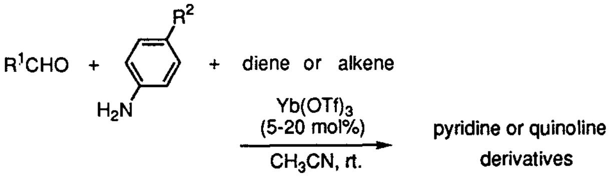
Table 3. Effects of Ln(OTf)$_3$ (1)

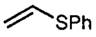
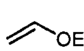
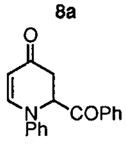
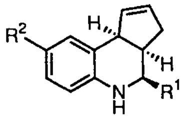
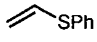
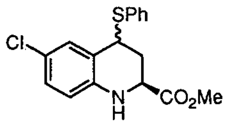
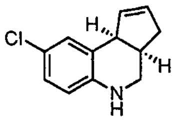


Ln	Yield (%)
Sc	94
Y	60
La	45
Pr	57
Nd	60
Sm	63
Eu	63
Gd	76
Dy	63
Ho	64
Er	97
Tm	92
Yb	85
Lu	72

hydroquinoline derivatives in high yields. Phenylglyoxal monohydrate reacted with amines and **2** or cyclopentadiene to give the corresponding tetrahydropyridine or quinoline derivatives in high yields. The imine derived from phenylglyoxal is known to be highly hygroscopic and its purification by distillation or chromatography is very difficult due to its instability.[6] Moreover, the three-component coupling reactions proceeded smoothly in aqueous solution, and commercial formaldehyde water solution could be used directly. Most lanthanide triflates tested were effective in the three-component coupling reaction (Table 5). These reactions provide very useful routes for the synthesis of pyridine and quinoline derivatives.

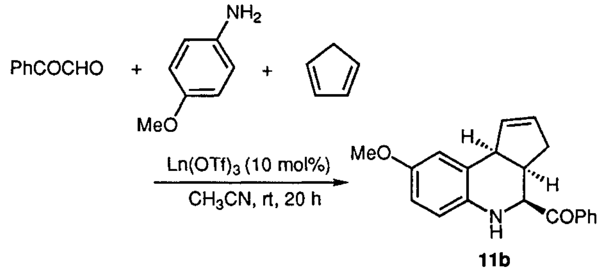
Table 4. One-Pot Syntheses of Pyridine and Quinoline Derivatives



R^1	R^2	Diene or Alkene	Product	Yield (%)
Ph	H	2	3a	80 (83)[a]
			6a	56
			7a	70
	Cl		7c	quant.
	H		8a	60
PhCO	H	2	 10	76
	H		 11a	94 (97)[b]
	OMe		11b	94
	Cl		11c	quant.
MeO$_2$C	H		12a	82
	Cl		12c	84
	Cl		 13	65
H[c]	Cl		 14	90[b]

a) Sc(OTf)$_3$ (10 mol%) was used. b) The reactions were carried out in aqueous solution (H$_2$O:EtOH:toluene = 1:9:4). c) Commercial formaldehyde water solution was used.

Table 5. Effects of Ln(OTf)$_3$ (2)



11b

Ln	Yield (%)
Sc	63
Y	77
La	88
Pr	75
Nd	97
Sm	91
Eu	87
Gd	91
Dy	87
Ho	76
Er	84
Tm	84
Yb	94
Lu	80

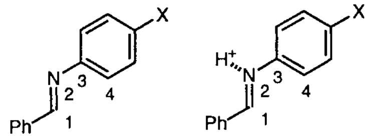
Reaction Mechanism

In the reactions of **1a**–**1c** with cyclopentadiene, a vinyl sulfide, or a vinyl ether (**1a**–**c** work as azadienes), **1a** or **1c** gave the best yields, while the yields using **1b** were lowest. The HOMO and LUMO energies and coefficients of **1a**–**c** and protonated **1a**–**c** are summarized in Table 6. These data do not correspond to the differences in reactivity between **1a**–**c**, if the reactions are postulated to proceed via concerted [4 + 2] cycloaddition. On the other hand, the high reactivity of **1a** and **1c** toward electrophiles compared to **1a** and **1b** may be accepted by assuming a stepwise mechanism.

We tested the reaction of **1a** with 2-methoxypropene in the presence of Yb(OTf)$_3$ (10 mol%). The main product was tetrahydroquinoline derivative **15a**, and small amounts of quinoline **16a** and β-amino ketone dimethylacetal **17a** were also obtained (Eq. 1). On the other hand, the three-component coupling reaction between benzaldehyde, aniline, and 2-methoxypropene gave only a small amount of tetrahydroquinoline derivative **15a**, and the main products in this case were β-amino ketone **18a** and its dimethylacetal **17a** (Eq. 2). Similar results were obtained in the reaction of **1b** with 2-methoxypropene and the three-component coupling reaction between benzaldehyde, anisidine, and 2-methoxypropene (Eqs. 3 and 4).

A possible mechanism of these reactions is shown in Scheme 1. Intermediate **19** is quenched by water and methanol generated in situ to afford **17** and **18**, respectively. While **15** is predominantly formed from **19** under anhydrous conditions, formation of **17** and **18** predominated in the presence of even a small amount of water. It is noted that these results suggest a stepwise mechanism in these types of imino Diels–Alder reactions.[14]

Thus, a new group of Lewis acids, lanthanide triflates, are quite effective for the catalytic activation of imines, and have achieved imino Diels–Alder reactions of imines with dienes or alkenes. The unique reactivities of imines which work as both dienophiles and azadienes under certain conditions have also been revealed. Three-component-coupling reactions between aldehydes, amines, and dienes or alkenes were successfully carried out using lanthanide triflates as catalysts to afford pyridine and quinoline derivatives in high yields. The triflates were

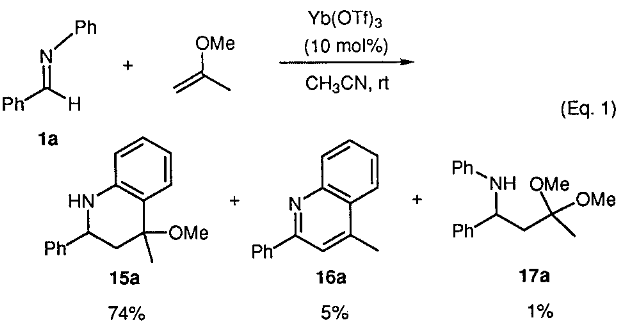


1a-c **1a-c-H$^+$**

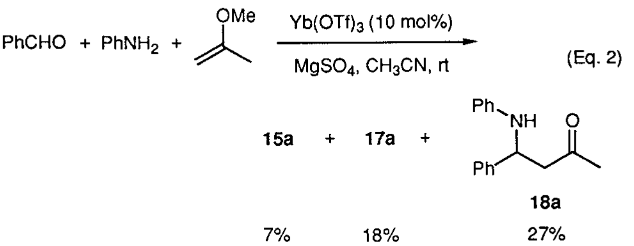
Table 6. HOMO and LUMO Energies and Coefficients of **1a-c**[a)]

	HOMO	Coefficient				LUMO	Coefficient			
	/eV	C1	N2	C3	C4	/eV	C1	N2	C3	C4
1a	-8.97	0.32	0.35	-0.34	-0.24	-0.69	0.43	-0.38	-0.30	0.27
1b	-8.68	0.32	0.29	-0.40	-0.24	-0.64	0.43	-0.38	-0.28	0.28
1c	-8.93	0.30	0.31	-0.35	-0.22	-0.85	0.43	-0.35	-0.33	0.27
1a - H$^+$	-13.19	0.15	0.31	-0.39	-0.19	-5.75	0.63	-0.48	-0.09	0.21
1b - H$^+$	-12.53	0.20	0.18	-0.46	-0.08	-5.58	0.62	-0.49	-0.07	0.21
1c - H$^+$	-12.58	0.16	0.15	-0.37	-0.10	-5.77	0.63	-0.47	-0.19	0.21

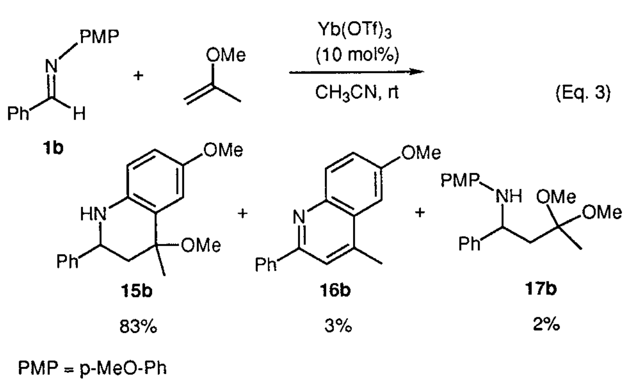
a) Calculated with MOPAC Ver 6.01 using the PM3 Hamiltonian. MOPAC Ver. 6, Stewart, J. J. P. *QCPE Bull.* **1989**, *10*, 9. Revised as Ver. 6.01 by Tsuneo Hirano, University of Tokyo, for HITAC and UNIX machines, *JCPE Newsletter*, **1989**, 10, 1.



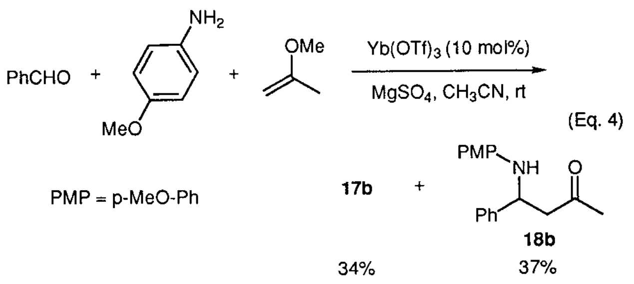
(Eq. 1)



(Eq. 2)



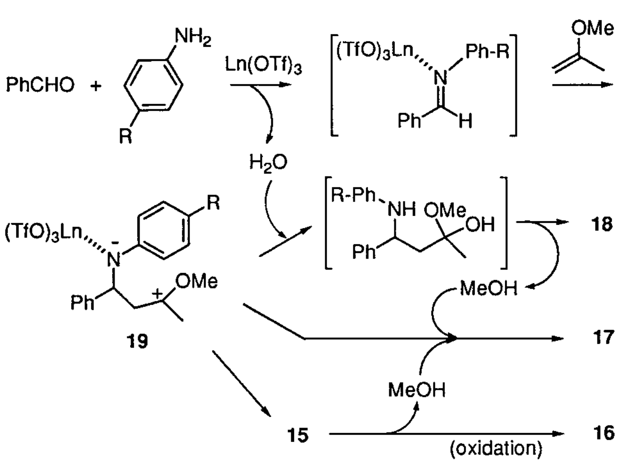
(Eq. 3)



(Eq. 4)

stable and kept their activity even in the presence of water and amines. According to these reactions, many substituted pyridines and quinolines can be prepared directly from aldehydes, amines, and dienes or alkenes. A stepwise reaction mechanism in these reactions was suggested from the experimental results. Further studies to develop new synthetic reactions using the properties of $Ln(OTf)_3$ are now actively in progress.

Melting points are uncorrected. IR spectra were recorded on a Horiba FT-300. ^{1}H NMR spectra were recorded on a JEOL JNM-EX270LFT-NMR system (270 MHz). Tetramethylsilane (TMS) served as an internal standard. Low- and high-resolution mass spectra were recorded on JEOL DX-303HF mass spectrometer. Column chromatography was performed on silica gel 60 (Merck) or Wakogel B5F. All reagents and solvents were used after purification according to usual methods. All new compounds gave satisfactory microanalyses or HRMS.



Scheme 1. A Possible Mechanism of the Three-component Coupling Reaction

Reactions of Imines with Dienes or Alkenes; Typical Procedure:
To a solution of $Yb(OTf)_3$ (0.05 mmol, 10 mol%) in MeCN (1.0 mL) was added *N*-benzilideneaniline (**1a**, 90.6 mg, 0.5 mmol) and **2** (129 mg, 0.75 mmol) in MeCN (1.5 mL) at r.t. The reaction mixture was stirred for 20 h, then sat. aq. $NaHCO_3$ (10 mL) was added and the product was extracted with EtOAc (10 mL × 3). After usual workup, the crude product was chromatographed on silica gel to afford **4a**; yield: 93%.

Three-Component Coupling Reaction; Typical Procedure:
To a suspension of $Yb(OTf)_3$ (31.0 mg, 0.05 mmol, 10 mol%) and $MgSO_4$ (400 mg, 3.32 mmol) in MeCN (0.5 mL) was added benzaldehyde (53.06 mg, 0.5 mmol) and aniline (0.5 mmol) in MeCN (1.5 mL), and then **1** (1.5 mmol) in MeCN (0.5 mL) at 0°C. After the mixture was stirred for 20 h at this temperature, water was added and the product was extracted with CH_2Cl_2. After usual workup, the crude product was chromatographed on silica gel to afford **3** (R^1 = Ph, R^2 = H) in an 80% yield.

1,2-Diphenyl-1,2,3,4-tetrahydropyridin-4-one (**3a**):[15]
IR (neat): $\nu = 1649, 1579\ cm^{-1}$.
^{1}H NMR ($CDCl_3$): δ = 2.77 (ddd, 1 H, J = 1.3, 3.3, 16.5 Hz), 3.29 (dd, 1 H, J = 7.3, 16.5 Hz), 5.27 (dd, 2 H, J = 0.99, 7.9 Hz), 6.98–7.34 (m, 10 H), 7.67 (dd, 1 H, J = 0.99, 7.6 Hz).
^{13}C NMR ($CDCl_3$): δ = 43.3, 61.4, 102.7, 118.3, 124.2, 125.9, 127.6, 128.8, 129.3, 137.7, 144.4, 148.1, 190.0.

1-(4-Methoxyphenyl)-2-phenyl-1,2,3,4-tetrahydropyridin-4-one (**3b**):
IR (neat): $\nu = 1649, 1579, 1213, 1036\ cm^{-1}$.
^{1}H NMR ($CDCl_3$): δ = 2.75 (ddd, 1 H, J = 0.99, 4.0, 16.5 Hz), 3.25 (dd, 1 H, J = 7.3, 16.5 Hz), 3.74 (s, 3 H), 5.18 (dd, 1 H, J = 4.0, 7.3 Hz), 5.22 (dd, 1 H, J = 0.99, 7.9 Hz), 6.80 (d, 2 H, J = 9.1 Hz), 6.95 (d, 2 H, J = 9.1 Hz), 7.22–7.33 (m, 5 H), 7.54 (dd, 1 H, J = 0.99, 7.9 Hz).
^{13}C NMR ($CDCl_3$): δ = 43.4, 55.4, 62.3, 101.5, 114.5, 121.0, 126.2, 127.7, 128.8, 138.1, 138.2, 149.5, 156.8, 189.9.

1-(4-Chlorophenyl)-2-phenyl-1,2,3,4-tetrahydropyridin-4-one (**3c**): mp 150°C.
IR (KBr): $\nu = 1643, 1574, 1091\ cm^{-1}$.
^{1}H NMR ($CDCl_3$): δ = 2.79 (dd, 1 H, J = 3.0, 16.5 Hz), 3.28 (dd, 1 H, J = 6.9, 16.5 Hz), 5.23 (dd, 1 H, J = 3.0, 6.9 Hz), 5.29 (d, 1 H, J = 7.6 Hz), 6.91–6.99 (m, 2 H), 7.22–7.36 (m, 7 H), 7.60 (d, 1 H, J = 7.6 Hz).
^{13}C NMR ($CDCl_3$): δ = 43.4, 61.7, 103.4, 119.7, 126.0, 127.9, 129.0, 129.5, 129.6, 137.5, 143.2, 147.7, 190.0.

4,5-Dimethyl-1,2-diphenyl-1,2,3,6-tetrahydropyridine (**4a**): mp 66 °C.

IR (KBr): ν = 2914, 1498 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.68 (s, 6 H), 2.37 (d, 1 H, J = 15.5 Hz), 2.80 (d, 1 H, J = 15.5 Hz), 3.48 (d, 1 H, J = 16.3 Hz), 3.74 (d, 1 H, J = 16.3 Hz), 5.04 (dd, 1 H, J = 2.3, 5.9 Hz), 6.7 (t, 1 H, J = 7.3 Hz), 6.84 (d, 2 H, J = 8.3 Hz).

^{13}C NMR (CDCl$_3$): δ = 16.5, 18.8, 37.0, 49.9, 56.2, 114.7, 117.8, 123.2, 123.5, 126.5, 126.8, 128.1, 129.1, 142.4, 149.4.

1-(4-Methoxyphenyl)-4,5-dimethyl-2-phenyl-1,2,3,6-tetrahydropyridine (**4b**):

^{1}H NMR (CDCl$_3$): δ = 1.62 (s, 3 H), 1.63 (s, 3 H), 2.35 (b, 1 H), 2.66 (b, 1 H), 3.43 (b, 1 H), 3.66 (b, 1 H), 3.73 (s, 3 H), 4.72 (m, 1 H), 6.48–7.46 (m, 9 H).

1-(4-Chlorophenyl)-4,5-dimethyl-2-phenyl-1,2,3,6-tetrahydropyridine (**4c**): mp 76 °C.

IR (KBr): ν = 1492, 1095 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.67 (s, 6 H), 2.36 (s, 1 H, J = 16.2 Hz), 2.80 (m, 1 H), 3.44 (d, 1 H, J = 16.2 Hz), 3.66 (d, 1 H, J = 16.2 Hz), 4.97 (dd, 1 H, J = 2.1, 6.1 Hz), 6.73 (d, 1 H, J = 9.2 Hz), 7.04–7.24 (m, 7 H).

^{13}C NMR (CDCl$_3$): δ = 16.5, 18.8, 37.0, 50.0, 56.4, 115.8, 122.5, 123.2, 126.7, 128.2, 128.3, 128.7, 128.9, 142.0, 148.0.

4-Methyl-2-phenyl-4-(2-propenyl)-1,2,3,4-tetrahydroquinoline (**5a**)

^{1}H NMR (CDCl$_3$): δ = 1.54 (s, 3 H), 1.59 (s, 3 H), 1.63 (m, 1 H), 2.18 (t, 1 H, J = 12.5 Hz), 4.02 (bs, 1 H), 4.40 (dd, 1 H, J = 2.5, 11.7 Hz), 4.99 (s, 3 H), 5.10 (s, 3 H), 6.51–7.45 (m, 9 H).

6-Methoxy-4-methyl-2-phenyl-4-(2-propenyl)-1,2,3,4-tetrahydroquinoline (**5b**):

IR (neat): ν = 3363, 1041 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.55 (s, 3 H), 1.59 (s, 3 H), 1.62–1.70 (m, 1 H), 2.18 (t, 1 H, J = 2.3, 11.9 Hz), 3.70 (s, 3 H), 3.83 (bs, 1 H), 4.44 (dd, 1 H, J = 2.3, 11.9 Hz), 4.98 (s, 1 H), 5.10 (s, 1 H), 6.48–7.46 (m, 8 H).

^{13}C NMR (CDCl$_3$): δ = 20.0, 30.1, 43.5, 44.0, 53.8, 55.9, 111.7, 113.6, 115.5, 126.7, 127.5, 128.6, 128.7, 139.0, 144.3, 151.3, 152.3.

6-Chloro-4-methyl-2-phenyl-4-(2-propenyl)-1,2,3,4-tetrahydroquinoline (**5c**):

^{1}H NMR (CDCl$_3$): δ = 1.51 (s, 3 H), 1.59 (s, 3 H), 1.62–1.67 (m, 1 H), 2.14 (t, 1 H, J = 12.5 Hz), 4.04 (bs, 1 H), 4.44 (dd, 1 H, J = 2.6, 11.9 Hz), 5.01 (s, 1 H), 5.11 (s, 1 H), 6.70–7.44 (m, 8 H).

3,4,5,9b-Tetrahydro-3H-cyclopenta[c]quinoline (**6a**):[7] mp 120 °C.

IR (KBr): ν = 3354, 1477 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.75–1.84 (m, 1 H), 2.57–2.69 (m, 1 H), 2.99 (ddd, 1 H, J = 3.3, 8.9, 18.1 Hz), 4.10 (d, 1 H, J = 8.6 Hz), 4.61 (d, 1 H, J = 3.0 Hz), 5.63 (m, 1 H), 5.83 (m, 1 H), 6.52–6.79 (m, 2 H), 6.94–7.44 (m, 8 H).

^{13}C NMR (CDCl$_3$): δ = 31.4, 46.0, 46.3, 58.0, 115.9, 119.1, 126.0, 126.3, 126.4, 127.2, 128.4, 128.9, 130.3, 133.9.

8-Methoxy-3,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (**6b**):

IR (neat): ν = 3344, 1502 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.81 (dd, 1 H, J = 8.9, 16.2 Hz), 2.59–2.70 (m, 1 H), 2.88 (ddd, 1 H, J = 3.3, 8.9, 14.9 Hz), 3.75 (s, 3 H), 4.08 (d, 1 H, J = 8.9 Hz), 4.56 (d, 1 H, J = 3.0 Hz), 5.66 (m, 1 H), 5.83 (m, 1 H), 6.56–6.66 (m, 3 H), 7.27–7.46 (m, 5 H).

^{13}C NMR (CDCl$_3$): δ = 31.4, 45.8, 46.9, 55.7, 58.5, 112.4, 114.1, 116.7, 126.5, 127.1, 128.4, 130.6, 133.7, 139.5, 142.9, 153.0.

8-Chloro-3,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (**6c**): mp 150 °C.

IR (KBr): ν = 3367, 1489 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.76–1.85 (m, 1 H), 2.54–2.66 (m, 1 H), 2.98 (ddd, 1 H, J = 3.3, 8.9, 14.5 Hz), 3.75 (bs, 1 H), 4.05 (d, 1 H, J = 8.6 Hz), 4.59 (d, 1 H, J = 4.3 Hz), 5.66 (m, 1 H), 5.79 (m, 1 H), 6.53 (d, 1 H, J = 8.6 Hz), 6.92 (dd, 1 H, J = 2.3, 8.6 Hz), 7.01 (d, 1 H, J = 2.3 Hz), 7.20–7.43 (m, 5 H).

^{13}C NMR (CDCl$_3$): δ = 31.4, 45.7, 46.3, 58.0, 117.0, 123.4, 126.2, 126.4, 127.4, 127.7, 130.9, 133.4, 142.4, 144.2.

2-Phenyl-4-phenylthio-1,2,3,4-tetrahydroquinoline (**7a**): *cis*/*trans* = 57/43; mp 41 °C.

IR (KBr): ν = 3383, 1601, 1490 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 2.09–2.28 (m, 1.4 H), 2.37 (ddd, 0.6 H, J = 2.8, 5.9, 13.0 Hz), 4.01 (bs, 1 H), 4.36 (dd, 0.6 H, J = 2.8, 11.1 Hz), 4.54 (t, 0.4 H, J = 3.1 Hz), 4.63 (dd, 0.6 H, J = 5.9, 11.1 Hz), 4.87 (t, 0.4 H, J = 7.1 Hz), 6.48–6.76 (m, 2 H), 7.01–7.72 (m, 12 H).

^{13}C NMR (CDCl$_3$): δ = 36.1, 40.1, 45.5, 45.9, 51.6, 57.0, 114.7, 117.3, 117.9, 118.6, 120.6, 126.3, 126.8, 127.0, 127.3, 127.4, 127.7, 127.8, 128.1, 128.5, 128.6, 128.9, 129.0, 129.3, 130.8, 131.9, 132.3, 134.9, 135.1, 143.1, 143.5, 144.9, 145.3.

6-Chloro-2-phenyl-4-phenylthio-1,2,3,4-tetrahydroquinoline (**7c**): *cis*/*trans* mixture; mp 169 °C.

IR (KBr): ν = 3390, 1680, 1493, 1238 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 2.04–2.22 (m, 1.3 H), 2.34 (ddd, 0.7 H, 2.0, 5.9, 13.2 Hz), 3.94–4.20 (bs, 1 H), 4.30 (dd, 0.7 H, J = 2.6, 11.2 Hz), 4.41 (t, 0.3 H, J = 2.8 Hz), 4.49 (dd, 0.7 H, J = 4.9, 5.9 Hz), 4.81 (dd, 0.3 H, J = 4.0, 10.2 Hz), 6.38, 6.95, 7.15–7.47 (m, 13 H).

^{13}C NMR (CDCl$_3$): δ = 35.6, 39.6, 45.2, 45.6, 51.6, 56.8, 115.7, 122.1, 122.2, 126.7, 127.3, 127.6, 127.8, 127.9, 128.2, 128.4, 128.6, 128.2, 128.9, 129.1, 130.1, 132.3, 12.7, 134.2, 142.6, 143.8.

8-Methoxy-2-phenyl-4-phenylthio-1,2,3,4-tetrahydroquinoline (**7d**): *cis*/*trans* mixture.

IR (neat): ν = 3398, 1491, 1248 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 2.14 (dd, 0.5 H, J = 3.3, 7.3 Hz), 2.24–2.39 (m, 1.5 H), 3.80 (s, 3 H), 4.37 (dd, 0.5 H, J = 2.6, 10.9 Hz), 4.54 (bs, 0.5 H), 4.58–4.87 (m, 2 H), 6.67–6.72 (m, 2 H), 7.21–7.42 (m, 11 H).

^{13}C NMR (CDCl$_3$): δ = 36.2, 40.1, 45.2, 45.7, 51.3, 55.4, 55.5, 56.6, 108.4, 108.5, 116.0, 116.6, 118.4, 120.5, 121.2, 122.7, 126.4, 126.7, 126.9, 127.0, 127.2, 127.4, 127.6, 127.7, 128.6, 128.8, 129.0, 131.9, 132.1, 135.0, 135.1, 135.2, 135.4, 143.3, 143.6, 146.2.

4-Ethoxy-2-phenyl-1,2,3,4-tetrahydroquinoline (**8a**): *cis*/*trans* mixture.

IR (neat): ν = 3383, 1608 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.22–1.29 (m, 3 H), 2.13 (t, 1 H, J = 11.2 Hz), 2.36–2.44 (m, 1 H), 3.50–3.75 (m, 2 H), 3.92 (bs, 1 H), 4.52 (dd, 1 H, J = 2.6, 11.2 Hz), 4.81 (dd, 1 H, J = 5.6, 10.4 Hz), 6.49–6.76 (m, 2 H), 7.01–7.47 (m, 7 H).

^{13}C NMR (CDCl$_3$): δ = 15.6, 37.1, 55.9, 63.5, 74.0, 114.0, 117.8, 112.6, 126.6, 127.2, 127.8, 128.2, 143.7, 144.6.

4-Ethoxy-6-methoxy-2-phenyl-1,2,3,4-tetrahydroquinoline (**8b**): *cis*/*trans* = 67/33.

IR (neat): ν = 3361, 1500 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.25 (t, 3 H, J = 6.9 Hz), 2.04 (ddd, 1 H, J = 10.8, 12.0, 12.2 Hz), 3.38 (ddd, 1 H, J = 2.6, 3.2, 12.2 Hz), 3.53–3.76 (m, 2 H), 3.75 (s, 3 H), 4.43 (dd, 1 H, J = 2.6, 12.0 Hz), 4.80 (dd, 1 H, J = 5.9, 10.8 Hz), 6.44–6.76 (m, 2 H), 7.04 (d, 1 H, J = 2.3 Hz), 7.28–7.44 (m, 5 H).

^{13}C NMR (CDCl$_3$): δ = 15.7, 37.2, 55.8, 56.2, 63.3, 74.1, 112.3, 114.9, 115.3, 123.7, 126.6, 126.9, 127.7, 128.5, 128.6, 138.9, 143.8, 152.4.

6-Chloro-4-ethoxy-2-phenyl-1,2,3,4-tetrahydroquinoline (**8c**): *cis*/*trans* mixture.

IR (neat): ν = 3388, 1460, 1300, 1084 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.26 (t, 3 H, J = 6.9 Hz), 2.00 (ddd, 1 H, J = 10.9, 11.5, 12.3 Hz), 2.40 (ddd, 1 H, J = 2.6, 5.6, 12.3 Hz), 3.50–3.75 (m, 2 H), 3.93 (bs, 1 H), 4.49 (dd, 1 H, J = 2.6, 11.5 Hz), 4.7 (dd, 1 H, J = 5.6, 10.9 Hz), 6.41 (d, 1 H, J = 8.6 Hz), 6.95–6.99 (m, 1 H), 7.27–7.42 (m, 6 H).

^{13}C NMR (CDCl$_3$): δ = 15.6, 36.6, 55.8, 63.9, 73.6, 115.1, 122.3, 124.1, 126.5, 126.9, 127.9, 128.1, 128.6, 128.7, 128.9, 143.0, 143.2.

6-Methoxy-2,4-diphenyl-4-trimethylsiloxy-1,2,3,4-tetrahydroquinoline (**9**):

IR (neat): ν = 3377, 2956, 1267, 846 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 0.00 (s, 9 H), 2.12 (m, 2 H), 3.60 (s, 3 H), 4.12 (dd, 1 H, J = 7.1, 15.9 Hz), 4.26 (bs, 1 H), 4.73 (t, 1 H, J = 7.4 Hz), 6.42 (d, 1 H, J = 2.6 Hz), 6.59–6.62 (m, 1 H), 6.75–6.80 (m, 1 H), 7.20–7.1 (m, 10 H).

^{13}C NMR (CDCl$_3$): δ = 1.62, 14.0, 50.4, 53.2, 55.6, 115.5, 115.8, 116.1, 126.3, 126.4, 126.6, 127.3, 127.4, 128.2, 128.3, 140.3, 143.6, 147.5, 150.8.

2-Benzoyl-1-phenyl-1,2,3,4-tetrahydropyridin-4-one (**10**): mp 44 °C.

IR (KBr): ν = 1693, 1645, 1579 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 2.89 (dd, 1 H, J = 0.99, 16.8 Hz), 3.33 (dd, 1 H, J = 9.2, 16.8 Hz), 5.25 (d, 1 H, J = 8.0 Hz), 5.74 (d, 1 H, J = 8.0 Hz), 7.01–7.93 (m, 11 H).

^{13}C NMR (CDCl$_3$): δ = 38.5, 63.1, 101.5, 118.9, 124.8, 128.4, 129.1, 129.6, 133.0, 134.1, 144.4, 150.6, 188.1, 193.7.

4-Benzyloxy-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (**11a**): mp 149 °C.

IR (KBr): ν = 3384, 1685 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.85–1.94 (m, 1 H), 2.36–2.46 (m, 1 H), 3.32 (ddd, 1 H, J = 3.3, 8.9, 14.5 Hz), 4.19 (d, 1 H, J = 7.9 Hz), 5.05 (d, 1 H, J = 3.3 Hz), 5.55–5.73 (m, 2 H), 6.67–7.93 (m, 10 H).

^{13}C NMR (CDCl$_3$): δ = 31.5, 42.6, 46.9, 59.8, 115.9, 119.0, 126.6, 128.1, 128.5, 128.8, 133.3, 134.0, 135.5, 143.9, 199.3.

8-Methoxy-4-benzyloxy-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (**11b**): mp 148 °C.

IR (KBr): ν = 3384, 1685 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.88 (dd, 1 H, J = 8.9, 16.6 Hz), 2.34–2.43 (m, 1 H), 3.26 (m, 1 H), 3.73 (s, 3 H), 4.12–4.19 (m, 2 H), 4.96 (d, 2 H, J = 3.0 Hz), 5.55–5.71 (m, 2 H), 6.59–6.66 (m, 2 H), 7.44–7.92 (m, 5 H), ^{13}C NMR (CDCl$_3$): δ = 31.3, 42.2, 55.5, 60.0, 112.3, 113.7, 117.1, 127.2, 128.7, 129.8, 133.2, 133.6, 135.4, 157.6, 152.8, 199.3.

8-Chloro-4-benzyloxy-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (**11c**):[6] mp 174 °C.

IR (KBr): ν = 3388, 1679 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.87 (m, 1 H), 2.35 (m, 1 H), 3.30 (ddd, 1 H, J = 3.3, 8.9, 14.5 Hz), 4.12 (d, 1 H, J = 8.9 Hz), 4.46 (bs, 1 H), 5.01 (d, 1 H, J = 3.3 Hz), 5.57 (m, 1 H), 5.65 (m, 1 H), 6.60 (d, 1 H, J = 8.3 Hz), 6.92–7.00 (m, 2 H), 7.46–7.61 (m, 3 H), 7.89–7.93 (m, 2 H).

^{13}C NMR (CDCl$_3$): δ = 31.4, 42.3, 46.8, 59.5, 117.0, 123.2, 126.5, 127.4, 128.1, 128.2, 128.3, 128.8, 130.1, 133.4, 135.3, 142.5, 198.8.

4-Methoxycarbonyl-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (**12a**): mp 84 °C.

IR (KBr): ν = 3400, 1726 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 2.32–2.47 (m, 2 H), 3.32 (ddd, 1 H, J = 3.3, 8.9, 17.8 Hz), 3.79 (s, 3 H), 4.11 (d, 1 H, J = 3.3 Hz), 4.17 (bs, 1 H), 5.63–5.74 (m, 2 H), 6.62 (dd, 1 H, J = 0.99, 7.9 Hz), 6.72 (m, 1 H), 6.94–7.02 (m, 2 H).

^{13}C NMR (CDCl$_3$): δ = 32.6, 40.7, 46.3, 52.1, 56.4, 115.7, 119.2, 125.8, 126.4, 128.6, 129.2, 129.7, 134.1, 143.8, 172.3.

8-Chloro-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (**12c**): mp 131 °C.

IR (KBr): ν = 3381, 1724 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 2.49–2.61 (m, 2 H), 3.45 (ddd, 1 H, J = 3.3, 8.9, 17.8 Hz), 3.98 (s, 3 H), 4.24 (d, 1 H, J = 3.3 Hz), 5.85 (m, 2 H), 7.72 (d, 1 H, J = 8.3 Hz), 7.07–7.16 (m, 2 H).

^{13}C NMR (CDCl$_3$): δ = 32.5, 40.4, 46.2, 52.2, 56.2, 116.7, 123.5, 126.3, 127.4, 128.2, 130.2, 133.5, 142.4, 172.0.

6-Chloro-2-methoxycarbonyl-4-phenylthio-1,2,3,4-tetrahydroquinoline (**13**): mp 90–93 °C.

IR (KBr): ν = 3388, 1739 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 2.43–2.47 (m, 2 H), 3.75 (s, 3 H), 4.05 (m, 1 H), 4.41 (t, 1 H, J = 5.6 Hz), 4.47 (s, H), 6.53 (d, 1 H, J = 8.6 Hz), 7.00 (dd, 1 H, J = 2.3, 8.6 Hz), 7.27–7.45 (m, 6 H).

^{13}C NMR (CDCl$_3$): δ = 30.1, 44.2, 52.0, 52.4, 116.1, 120.6, 122.4, 127.7, 128.3, 128.5, 129.1, 129.7, 132.4, 141.8, 173.2.

8-Chloro-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline (**14**):

IR (neat): ν = 3398, 1495, 1095 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 2.14 (dd, 1 H, J = 1.5, 14.0 Hz), 2.59–2.85 (m, 3 H), 3.06 (dd, 1 H, J = 4.0, 10.2 Hz), 3.67 (bs, 1 H), 3.83 (d, 1 H, J = 4.6 Hz), 5.66–5.77 (m, 2 H), 6.44 (d, 1 H, J = 8.6 Hz), 6.90 (dd, 1 H, J = 2.0, 8.1 Hz), 7.08 (dd, 1 H, J = 0.8, 2.5 Hz).

^{13}C NMR (CDCl$_3$): δ = 35.7, 37.1, 44.5, 45.8, 116.1, 122.4, 126.1, 126.4, 129.0, 129.1, 135.1, 144.4.

4-Methoxy-4-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (**15a**): *cis/trans* mixture.

IR (neat): ν = 3377, 1487, 1315 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.53 (s, 3 H), 1.77–1.98 (m, 1 H), 2.38 (t, 1 H, J = 12.2 Hz), 3.09 (s, 3 H), 3.98 (bs, 3 H), 4.50 (dd, 1 H, J = 2.6, 12.2 Hz), 6.49–6.77 (m, 2 H), 7.01–7.52 (m, 7 H).

^{13}C NMR (CDCl$_3$): δ = 32.1, 40.3, 50.0, 55.8, 75.1, 114.3, 117.9, 126.5, 126.7, 126.8, 127.8, 128.0, 128.5, 128.6, 143.5.

4,6-Dimethoxy-4-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (**15b**): *cis/trans* mixture.

IR (neat): ν = 3365, 1284, 1234 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.51 (s, 3 H), 1.76–1.90 (m, 1 H), 2.15–2.21 (m, 1 H), 3.21 (s, 3 H), 3.74 (s, 3 H), 4.45 (dd, 1 H, J = 2.3, 12.2 Hz), 6.46–6.92 (m, 3 H), 7.26–7.48 (m, 5 H).

^{13}C NMR (CDCl$_3$): δ = 32.2, 40.4, 49.7, 55.5, 55.9, 75.4, 111.4, 114.9, 115.5, 125.6, 126.5, 128.5, 128.6, 139.4, 144.1, 152.5.

4-Methyl-2-phenylquinoline (**16a**):

IR (neat): ν = 3064, 1599 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 2.70 (d, 3 H, J = 0.66 Hz), 7.30–7.52 (m, 5 H), 7.66–7.69 (m, 2 H), 7.92–7.96 (m, 1 H), 8.12–8.18 (m, 3 H).

^{13}C NMR (CDCl$_3$): δ = 18.9, 119.7, 123.5, 125.9, 127.2, 127.5, 128.7, 129.1, 129.2, 130.2, 139.7, 144.7, 148.1, 156.9.

6-Methoxy-4-methyl-2-phenylquinoline (**16b**): mp 132–134 °C.

IR (KBr): ν = 3060, 1117 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 2.70 (s, 3 H), 3.95 (s, 3 H), 7.18 (d, 1 H, J = 2.6 Hz), 7.35–7.53 (m, 4 H), 7.67 (s, 1 H), 8.06–8.12 (m, 3 H).

^{13}C NMR (CDCl$_3$): δ = 19.2, 55.5, 101.9, 120.0, 121.5, 127.3, 128.1, 128.7, 128.8, 131.8, 139.9, 143.3, 144.1, 154.8, 157.5.

3,3-Dimethoxy-1-(N-phenylamino)-1-phenylbutane (**17a**):

IR (neat): ν = 3381, 1045 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.40 (s, 3 H), 1.88 (dd, 1 H, J = 3.3, 14.2 Hz), 2.19 (dd, 1 H, J = 11.2, 14.2 Hz), 3.18 (s, 3 H), 3.29 (s, 3 H), 4.35 (dd, 1 H, J = 3.3, 11.2 Hz), 5.37 (bs, 1 H), 6.45 (dd, 2 H, J = 1.2, 8.7 Hz), 6.62 (t, 1 H, J = 7.3 Hz), 7.03–7.42 (m, 7 H).

^{13}C NMR (CDCl$_3$): δ = 20.9, 45.9, 48.0, 48.3, 56.2, 101.3, 113.5, 117.1, 126.1, 126.9, 128.7, 129.0, 144.9, 148.0.

3,3-Dimethoxy-1-[N-(4-methoxyphenyl)amino]-1-phenylbutane (**17b**):

IR (neat): ν = 3375, 1512, 1252 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 1.40 (s, 3 H), 1.84 (dd, 1 H, J = 3.1, 14.3 Hz), 2.19 (dd, 1 H, J = 11.2, 14.3 Hz), 3.17 (s, 3 H), 3.29 (s, 3 H), 3.67 (s, 3 H), 4.29 (dd, 1 H, J = 3.1, 11.2 Hz), 6.39–6.75 (m, 2 H), 7.22–7.56 (m, 7 H).

^{13}C NMR (CDCl$_3$): δ = 21.0, 45.8, 48.0, 48.3, 55.7, 56.9, 101.3, 114.5, 114.6, 127.1, 128.3, 129.0, 130.5, 143.5.

4-(N-Phenylamino)-4-phenylbutan-2-one (**18a**):[16]

IR (neat): ν = 3388, 1604 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 2.07 (s, 3 H), 2.90 (d, 2 H, J = 6.3 Hz), 4.40 (bs, 1 H) 4.83 (t, 1 H, J = 6.6 Hz), 6.52–6.68 (m, 3 H), 7.20–7.43 (m, 7 H).

^{13}C NMR ($CDCl_3$): δ = 30.6, 51.1, 54.3, 113.7, 117.8, 126.2, 127.3, 128.7, 129.1, 142.4, 146.7, 207.1.

4-[N-(4-Methoxyphenyl)amino]-4-phenylbutan-2-one **(18b)**:[17]

IR (neat): ν = 3361, 1612, 1242 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.08 (s, 3 H), 2.88 (d, 2 H, J = 6.7 Hz), 3.67 (s, 3 H), 3.93 (bs, 1 H), 4.76 (t, 1 H, J = 6.7 Hz), 6.48–6.74 (m, 4 H), 7.19–7.40 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 30.7, 51.3, 55.0, 55.3, 114.7, 115.3, 127.2, 127.4, 128.7, 141.0, 142.8, 152.3, 207.2.

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